

INVESTIGATING THE 3.3 μm INFRARED FLUORESCENCE FROM NAPHTHALENE FOLLOWING ULTRAVIOLET EXCITATION

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ABSTRACT

Polycyclic aromatic hydrocarbon (PAH) type molecules are proposed as the carriers of the unidentified infrared (UIR) bands. Detailed studies of the 3.3 μm infrared emission features from naphthalene, the simplest PAH, following ultraviolet laser excitation are used in the interpretation of the 3.29 μm (3040 cm^{-1}) UIR band. A time-resolved Fourier transform spectrometer is used to record the infrared emission spectrum of gas-phase naphthalene subsequent to ultraviolet excitation facilitated by an excimer laser operated at either 193 nm or 248 nm. The emission spectra differ significantly from the absorption spectrum in the same spectral region. Following 193 nm excitation the maximum in the emission profile is red-shifted 45 cm^{-1} relative to the absorption maximum; a 25 cm^{-1} red-shift is observed after 248 nm excitation. The red-shifting of the emission spectrum is reduced as collisional and radiative relaxation removes energy from the highly vibrationally excited molecules. Coupling between the various vibrational modes is thought to account for the differences between absorption and emission spectra. Strong visible emission is also observed following ultraviolet excitation. Visible emission may play an important role in the rate of radiative relaxation, which according to the interstellar PAH hypothesis occurs only by the slow emission of infrared photons. Studying the visible emission properties of PAH type molecules may be useful in the interpretation of the DIBs observed in absorption.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are thought to be present in the interstellar medium (ISM) and are the proposed molecular carriers of the unidentified infrared (UIR) bands observed in many astronomical objects (Puget and Leger 1989; Allamandola, Tielens, and Barker 1989). The UIR bands are a group of spectral features commonly seen together in the infrared emission spectra of astronomical objects. PAH type molecules are believed to be responsible for these UIR bands due to the qualitative similarities between the UIR bands and the infrared absorption spectra of many PAH type molecules. According to the interstellar PAH hypothesis, PAH's become vibrationally excited following the absorption of an ultraviolet photon and subsequent internal conversion of that electronic energy into vibrational excitation.

One of these UIR bands, the $3.29\text{ }\mu\text{m}$ (3040 cm^{-1}) UIR band is thought to be a $v=1 \rightarrow v=0$ C-H stretching transition in a PAH type molecule. However, this band is red-shifted approximately 30 cm^{-1} relative to the $v=0 \rightarrow v=1$ transition observed in the absorption spectrum of naphthalene. A more quantitative comparison is made when the infrared emission spectrum of a vibrationally excited naphthalene is compared with the $3.3\text{ }\mu\text{m}$ (3040 cm^{-1}) UIR band. A number of laboratories are studying the infrared emission from gas-phase PAH's following ultraviolet laser excitation (Shan, Suto, & Lee 1991; Brenner & Barker 1992; Cook, Schlemmer, & Saykally 1993).

The experiments reported here measure both wavelength-resolved and time-resolved infrared emission spectra of naphthalene following 193 nm and 248 nm excitation using an FTIR. The spectra presented are recorded at a resolution of $\approx 10\text{ cm}^{-1}$. The emission spectra differ significantly from the gas phase absorption spectrum, and the emission spectra more closely resemble the UIR bands in the $3.3\text{ }\mu\text{m}$ region than the absorption spectrum. The maximum of the emission profile is red-shifted relative to the absorption maximum and the emission profile is notably asymmetric with a tail extending to the red of the maximum. Moreover, the extent of the band shift is strongly dependent on the excitation laser wavelength. Thus, the magnitude of the frequency shift increases as the amount of internal vibrational energy of the molecule increases.

EXPERIMENTAL

Only a brief description of the apparatus will be given here; for a detailed description see, Williams & Leone 1994 and for an overview of the time-resolved Fourier transform spectroscopic (FTS) technique see, Rogers & Leone 1994. Gas-phase naphthalene is introduced into the vacuum chamber through a heated copper tube which is connected to a heated external container which houses the naphthalene sample. The effusive source of naphthalene condenses onto a liquid nitrogen cold trap which is positioned approximately 10 cm from the inlet tube; no pressure rise is detected when naphthalene is flowing into the chamber. A continuous flow of argon is directed onto the inner surfaces of the entrance and exit windows of the chamber to eliminate the formation of carbonaceous deposits; as a result the background pressure during a typical experiment is 40 Pa. An excimer laser, operating at either 193 nm or 248 nm, is used as the excitation source. Laser fluences are maintained such that there is a linear dependence of the fluorescence intensity with laser power. Fluorescence is collected by an $f/2$ CaF_2 lens and is imaged into the FTS. Infrared spectra are recorded in emission at a resolution of 10 cm^{-1} through a bandpass filter by an LN_2 cooled InSb detector. Three different time-resolved spectra are recorded at delays of 6.8 μs , 22.6 μs , and 38.4 μs following the triggering of the excitation laser.

Strong visible emission following ultraviolet excitation is easily noticed by visual inspection. Visible emission following 193 nm excitation appears reddish, following 248 nm excitation the emission appears to be blue. Our present apparatus is optimized only for studies in the mid infrared region and is therefore not well suited to study visible emission. However, by fitting the spectrometer with a silicon photodiode detector it is possible to measure the transient behavior of the visible emission and to measure some

spectral features. We do not present a visible emission spectrum due to the large differences in instrument response in the region of interest which may introduce artificial spectral features into the spectral. The current Fourier transform spectrometer will be modified in the near future to allow coverage in this spectral region.

RESULTS/DISCUSSION

The result of the laser excitation process is to produce an ensemble of vibrationally excited naphthalene molecules. At short time, $<1\ \mu\text{s}$, we assume the initial average energy of the excited naphthalene is equal to the sum of the photon energy and the initial thermal vibrational energy of naphthalene ($\langle E_{\text{vib}} \rangle$). At an inlet tube temperature of 350 K, $\langle E_{\text{vib}} \rangle = 1440\ \text{cm}^{-1}$. The ensemble of molecules produced by the laser has a narrow energy distribution centered about $42,000\ \text{cm}^{-1}$ or $53,000\ \text{cm}^{-1}$ for 248 nm and 193 nm excitation, respectively. As collisions remove energy from the highly excited molecules, the energy distribution broadens and shifts to lower energy.

Figure 2 shows a transient infrared emission trace from naphthalene following 193 nm excitation, it is an average of 250 laser pulses, and is recorded by a 1.27 cm diameter 77K InSb detector fitted with a bandpass filter ($3.0 - 4.2\ \mu\text{m}$), with no argon flowing in the cell at the time of the experiment.

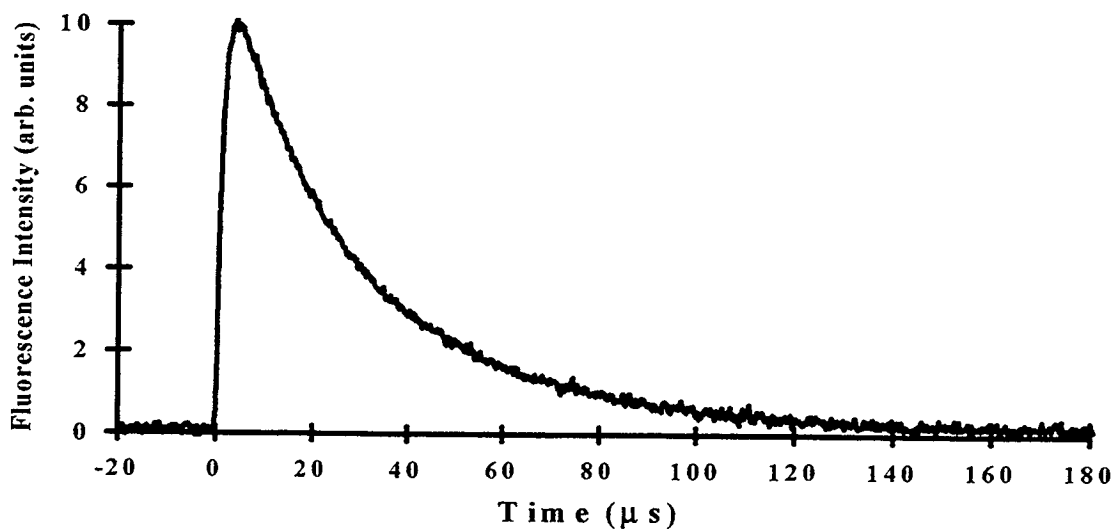


Figure 2. Transient infrared emission trace from gas-phase naphthalene following 193nm excitation; see text for details.

The trace in figure 2 does not exhibit a simple single exponential decay, nor does it exhibit the slow rate of emission which might be predicted by the known rate of spontaneous emission of a C-H stretching transition in an aromatic molecule. This rate should be approximately $10 - 100\ \text{sec}^{-1}$ (Reddy, Heller, & Berry 1982). The rapid rate of fluorescence may be due to several factors; quenching by naphthalene and/or argon, molecular diffusion out of the observation region of the apparatus, or an increase in the rate of spontaneous emission induced by other intramolecular processes. The first two factors can be checked by changing experimental conditions such as the background

pressure of argon, and using a larger active area detector. The temporal characteristics of the emission do not change significantly upon changing these conditions (except at high argon pressures where collisional deactivation is significant), suggesting that there may indeed be an increase in the rate of spontaneous emission induced by other intramolecular processes. This hypothesis is made even more plausible by noting that the rate of visible emission is only a factor of three faster than the infrared emission which might imply some correlation between the infrared and visible emission rates. This would have an important impact on the interstellar PAH hypothesis.

Vibrationally excited interstellar PAH type molecules are thought to relax only by emission of infrared photons. This slow rate of spontaneous emission plays an important role in determining the chemical composition of the proposed carriers of the UIR bands. There is a competition between the rate of radiative deactivation and the rate of unimolecular decomposition which determines the chemical nature of interstellar molecules. A smaller molecule will undergo unimolecular decomposition faster than a larger molecule excited to the same energy. Visible luminescence from excited PAH molecules may rapidly increase the rate of radiative relaxation. The visible emission from naphthalene decays on a time scale of $\approx 25 \mu\text{sec}$.

Figure 3 shows a comparison of the wavelength resolved IR emission spectra recorded $6.8 \mu\text{s}$ after 193 nm and 248 nm excitation; also shown for reference is the absorption spectrum of naphthalene in this region.

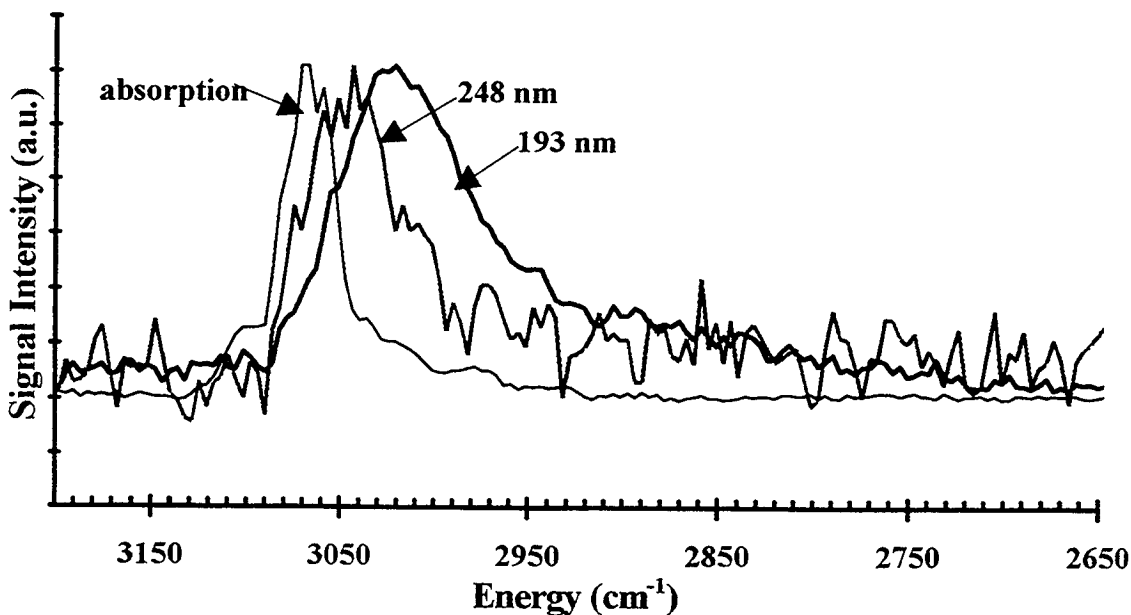


Figure 3. Infrared emission spectra from gas-phase naphthalene in the C-H stretching region, $6.8 \mu\text{s}$ after 193 nm and 248 nm excitation. The peak amplitudes have been normalized to one another.

The IR emission spectrum recorded at $6.8 \mu\text{s}$ after the 193 nm excitation ($53,000 \text{ cm}^{-1}$ internal energy content) shows a 45 cm^{-1} red-shift relative to the maximum observed

in the IR absorption spectrum; for 248 nm excitation ($42,000\text{ cm}^{-1}$) the red-shift is reduced to 25 cm^{-1} . In addition to the shift of the profiles in emission, a pronounced asymmetry is observed extending to the red of the maximum. There is no observable structure in the asymmetric tail of the emission profiles, such as anharmonically shifted $\Delta v = -1$ transitions. The data for the 248 nm excitation has less signal-to-noise than the 193 nm data; this is primarily due to the reduced absorption cross section and the lower laser fluences employed. At the longer time delays ($22.6\text{ }\mu\text{s}$ and $38.4\text{ }\mu\text{s}$) the maximum in the emission profile gradually approaches the maximum in the absorption profile. In addition to the shift of the emission maximum, the asymmetry of the emission profile also decreases.

The high extent of vibrational excitation in the emitting molecules is largely responsible for the observed deviation of the emission spectra relative to the absorption spectrum. Due to the rather anharmonic C-H stretching potential it is reasonable to assume that interactions with other vibrations will influence the spectroscopy in the $3.3\text{ }\mu\text{m}$ region. These interactions can be thought of in terms of anharmonic coupling between various vibrational modes. In general, the fundamental frequency of a C-H stretch, labeled as ν_{CH} , is strongly affected by excitation of the lower frequency modes in the molecule, labeled as ν_{LF} . If there is an interaction which couples one vibrational mode to another, then the frequency of one may be perturbed by the other, so that $(\nu_{\text{CH}} + \nu\nu_{\text{LF}})' - \nu\nu_{\text{LF}} \neq \nu_{\text{CH}}$, where $\nu = 0, 1, 2, 3, 4, \dots$. Herzberg (1968) defines this as a sequence of difference bands, or simply as sequence bands. In the case of naphthalene, these interactions shift the observed C-H stretching frequency to a lower value and greatly reduces the probability of observing any resolvable features in the emission spectrum.

If the $3.3\text{ }\mu\text{m}$ UIR band results from a C-H stretching transition in a polyatomic molecule excited by UV light, the lack of significant asymmetry in its emission profile and the presence of resolvable features to the red of the emission maximum suggests that it is not comprised of sequence bands. Also, if the resolvable UIR band at $3.4\text{ }\mu\text{m}$ (2940 cm^{-1}) is a $\Delta v = -1$ transition originating from $v = 2$ in a C-H stretch as proposed, then this implies two things: 1) there is sufficient internal vibrational energy to excite $v = 2$ in a C-H stretch, and 2) the fact that this feature is resolvable suggests sequence bands are not congesting the spectrum. An apparent lack of sequence bands in the region of the $3.3\text{ }\mu\text{m}$ UIR band may provide information about lower frequency vibrational modes in the carrier molecules. For instance, if the carrier of the $3.3\text{ }\mu\text{m}$ UIR band possesses a large number of highly excited low frequency modes, then it might be expected that emission from a C-H stretching vibration would be affected by the excitation in the low frequency modes. It also could be argued that the molecules responsible for the $3.3\text{ }\mu\text{m}$ UIR feature may not contain the number of excited low frequency modes that are expected in a typical PAH type molecule following ultraviolet excitation. Questions which still need to be addressed include: do the IR emission characteristics of PAH type molecules change upon ionization and how would partial de-hydrogenation effect the emission characteristics and frequencies of PAH type molecules? It is clear that a greater range of PAH type

molecules must be studied to identify trends that can elucidate the complex nature of the interactions between various vibrational modes.

CONCLUSION

Wavelength-resolved and time-resolved infrared emission spectra in the $3.3\ \mu\text{m}$ ($3030\ \text{cm}^{-1}$) region from naphthalene following UV laser excitation are measured. Emission spectra from naphthalene initially excited to $42,000\ \text{cm}^{-1}$ or $53,000\ \text{cm}^{-1}$ differ significantly from spectra observed in absorption. The observed red-shifting of the maximum in the emission spectra relative to the maximum observed in the absorption spectra is attributed to a sequence of difference bands. The apparent lack of any resolvable features near $3.40\ \mu\text{m}$ ($2940\ \text{cm}^{-1}$) suggests that neutral, fully hydrogenated naphthalene is not responsible for the emission spectra observed from interstellar objects which possess features at $3.40\ \mu\text{m}$ ($2940\ \text{cm}^{-1}$). Coupling between the various vibrational degrees of freedom has been discussed within the context of the interstellar PAH hypothesis. The complete IR emission spectra of various neutral PAH's and their ionic counterparts excited with various wavelengths should be investigated to provide additional insight on the interstellar PAH hypothesis. Visible emission from PAH's has been observed and is discussed in terms of possibly greatly increasing the proposed rate of radiative relaxation of highly excited molecules.

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